朝比奈泰彦*: 地衣類雑記 (§ 254)

Yasuhiko ASAHINA*: Lichenologische Notizen (§ 254)

§ 254. **Microchemical treatment of the subspecies of *Usnea bayleyi* (Stirt.) Zahlbr.**

To distinguish three subspecies[1] of *U. bayleyi* (Stirt.) Zahlbr. microchemically, the following procedure is adopted conveniently. Though the type specimen of *Usnea* (Eumitria) *chrysopoda* Stein. was collected in Philippines, this species occurs very frequently in Australia and New Guinea. The thallus of the subsp. *chrysopoda* is colored pure yellow, corresponding to its medullary color. The herbarium specimens of the subsp. *bayleyi* are colored somewhat sordid stramineous and those of subsp. *septentrionalis*[2] sordid dark grayish, the medullary layers of the latter two subspecies being rosy colored.

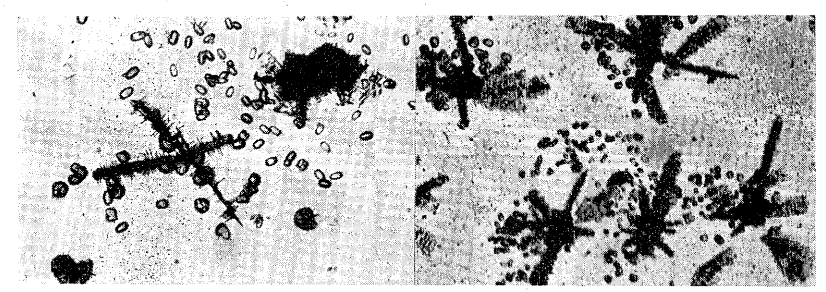


Fig. 1. Kernel-like crystals of eumitrins and lamellar crystals of usnic acid.

Digested with cold benzene subsp. *chrysopoda* gives a yellow solution, which on evaporation leaves a viscous syrup. Recrystallized from GE-solution under cover glass, the latter yields thin lamellar crystals of usnic acid mixed with kernel-like crystals of eumitrins (Fig. 1).

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1) J. J. B. 42: 5–7, 1967.

2) Thalli attaining often a length of up to 30 cm in the Himalayan districts.

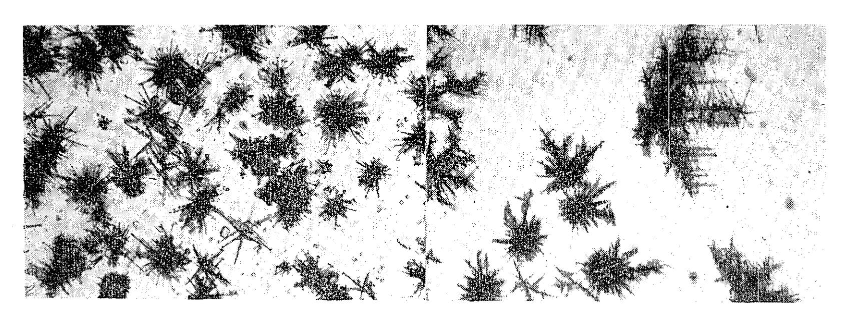


Fig. 2. Crystals of the so-called 'materia rubra', in cold benzene easily soluble pigment. (cf. Asahina, Lichens of Japan, III, p. 40, fig. 31, 1956).

On the contrary the cold benzene extract of *U. bayleyi* subsp. *septentrionalis* Asah. is colored deep red. On evaporation there remains a dark red resinous substance, which on recrystallization from GE, we obtain a crowd of druses of the so-called "materia rubra",[3] dispersed with some amounts of eumitrin crystals and usnic acid (Fig. 2). Also the benzene extract of the subsp. *bayleyi* is colored red and yields on recrystallization from GE, elongated crystals of usnic acid mixed with kernel-like crystals of eumitrins and sometimes a few crystal aggregates of "materia rubra."[3] The same lichen chips, which were extracted with cold benzene, was put in contact with ether for several minutes and the ether evaporated on a slide glass. This ether extract contains in general a depside and a fatty acid such as barbatic acid and caperatic acid, and if necessary they may be identified by the thin-layer chromatography.

At last the thalline rest is extracted with hot acetone, by which a red colored solution is obtained. On evaporation upon a slide glass the latter yields reddish stained white crystalline substance.

A chromatogram of the above mentioned acetone extract is shown by Fig. 6 of J. J. B. **40**: 176 (1965), hereat we need to make a correction that "B....materia rubra" must be changed to "B....acetone soluble red pigment." The so-called "materia rubra" does not ascend the glass plate coated with silicagel G and is retained at the starting point.

In the herbarium of the writer, there is a specimen, which should be

3) The so-called "materia rubra" is the crystal druse formed by radiately congregated spindle-shaped crystals.

identified with *U. chrysopoda* Stein. It was collected by E. Matuda on Monte Ovando, Chiapas, Mexico on Jan. 1, 1925, contained usnic acid and eumitrins. Another Eumitria specimen collected by Matuda in Mexico, which the writer identified with *U. perplectata* Mot. contained usnic and diffractaic acids, but not eumitrins. An African specimen collected by des Abbayes in French Guinea and determined by Motyka as *Usnea* (Eumitria) *implicita* (Stirt.) Zahlbr. contained also in benzene extract usnic acid, eumitrins and a moderate quantity of the "materia rubra" and in acetone extract norstictic acid.

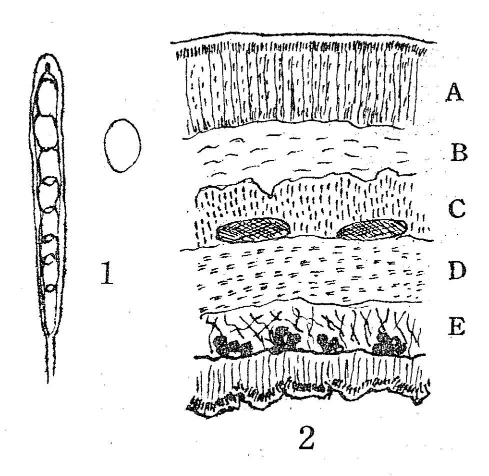


Fig. 3. Vertical section of apothecium of *U. bayleyi* subsp. *septentrionalis* Asah. (specimen collected in Sikkim; Pamianchi no. 2, 1960), 1. Ascus and spores (spore: ellipsoid, 8-10×5-6 μ large). 2-A. Hymenium. B. Hypothecium. C. Central medullary layer containing fibrous tissues. D. Central medullary layer containing rosy matters. E. Gonidial layer.

In this occasion the writer has the pleasure to announce the chemical constitution of eumitrins, which was recently elucidated by Shibata and his coworkers.[4] Sometime ago Nuno[5] isolated the eumitrin fractions A and B. Shibata and others have separated eumitrin A (sensu Nuno) in eumitrin A_1 and A_2. These eumitrins are the derivatives of double anthraquinole- or anthrone-derivatives, resembling skyrin,[6] rugulosin,[7] and flavo-obscurin.[8]

EUMITRIN A_1 EUMITRIN A_2 EUMITRIN B

4) Tetrahedron **29**: 519-528, 1973.
5) J. J. B. **46**: 294, 1971.
6) J. J. B. **43**: 340, 1968.
7) J. J. B. **43**: 340-341, 1968.
8) J. J. B. **43**: 343, 1968.

本雑記 §203 で発表したように筆者は *Usnea chrysopoda* と *U. bayleyi* とを同一種に併合し其内容物の差異で之を 3 種の subspecies に分割した。従て是等の亜種を区別する為には顕微化学的の操作が必要である。之を略記すると次の通りである。

Subsp. *chrysopoda* は地衣体の表面が清潔な黄色を呈する，その少量の枝条を丸めてミクロ浸出管に入れ冷ベンゼンを注加し暫時振盪すると純黄色の液を生じ，これをスライドの上に広げて蒸発乾涸して生する粘稠のエキスをかきとり別のスライド上で G. E. を加へてカバーグラスで覆い加熱して再結晶するとウスニン酸の長板晶とユーミトリンの顆粒晶が出る。

Subsp. *septentrionalis* の冷ベンゼン浸出液は暗紅色を呈しその蒸発残渣を G. E. から再晶すると先づ暗褐色の放射性簇晶（所謂 materia rubra）が先づ出現し，その後にウスニン酸とユーミトリンの結晶が析出してくる。

Subsp. *bayleyi* の冷ベンゼン浸出液は紅色を呈し，その蒸発残渣を G. E. から再晶するとウスニン酸とユーミトリンの結晶が主として析出するが同時に materia rubra の簇晶も出現するが其量は subsp. *septentrionalis* に比ぶれば遙に少ない。その多少は赤道を遠ざかって北上するに従て増加し，台湾でも已に *septentrionalis* に近いものがあり日本内地やヒマラヤ産のものは殆どすべてが *septentrionalis* に属する。

「ユーミトリン」は最近柴田教授及協力者によって其構造が決定された。先に布[5]はユーミトリンを A と B との二種に分離したが柴田教授及其協力者は布の A を A_1, A_2 とに分離し，これと B とを合せて三種のユーミトリンの構造を前記の如く決定した。これによるとユーミトリン類は絲状菌の代謝産物 skyrin, rugulosin 又は flavo-obscurin 等によく似た重複アントラキノール又は重複アントロン誘導体である。尚此のユーミトリンを溶出した地衣体をエーテルで冷浸しその乾燥残渣を集めて G. E. から再結晶するとバルバチン酸とカペラット酸（又はプロトリヘステリン酸系の脂肪酸）が出る。最後に残った地衣体を熱アセトンで抽出し，その溶液をスライド上で蒸発し残渣を検すると多くの場合ノルスチクチン酸（サラチン酸含有）であり稀にプロトセトラール酸が現われる。

□A. S. Hitchcock : **Manual of grasses of the United States.** 2nd ed. revised by Agnes Chase in 2 Vols. Dover Pub. Inc., New York. Each Vol. $ 4.00. 5×24 cm.　この本は有名なヒッチコック氏の北米合衆国のイネ科植物の便覧で，1935 年に出版されたものを，1950 年に Agnes Chase 氏が改訂した覆刻版で，1950 年版そのままである。今日ではそれがたやすく入手できないか，できても高価なためか，とにかく流行の覆刻版として出たものである。内容には全く手を入れないで 1-569 頁までを 1 巻とし，570-1051 頁までを 2 巻として全 2 巻の形式をとったものである。表紙は厚紙であるが製本は堅牢であるから使用に便利である。　（久内清孝）